Supporting Information

Single-molecule conductance of pyridine-terminated dithienylethene switch molecules

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Synthesis

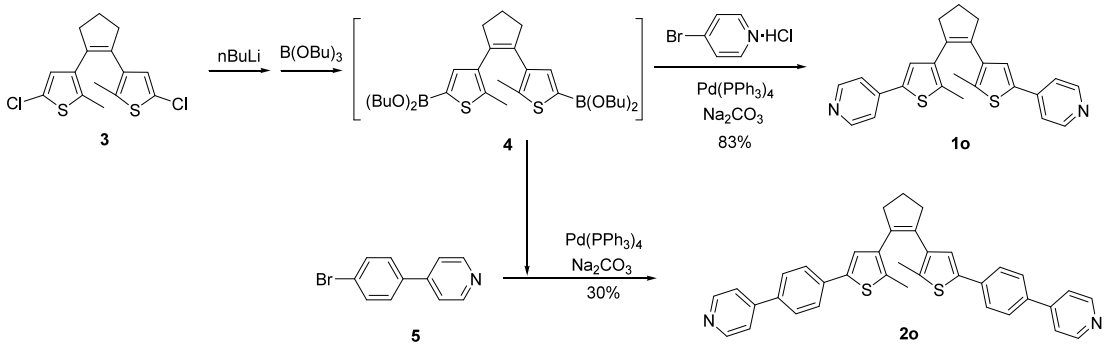

Fig. S1. Steps in the synthesis protocols, described in detail in the *Methods* section of the main text.

Additional Experimental Details

As verification of the ability of our apparatus to produce results consistent with those published previously, we measured several molecules studied by Venkataraman and collaborators. In Fig. S2 we show results for four diaminoalkanes (with 3, 4, 10, and 12 carbons). The conductance values we obtain are in good agreement with the previous measurements.[1] A linear fit to log(*G*) as a function of the number of methylene groups yields a conductance decay constant of 0.91 ± 0.03 per methylene group, which is in excellent agreement with the value reported by Venkataraman *et al.*[1] These data also show that we are able to measure conductance values as low as 1×10^{-6} G_0.

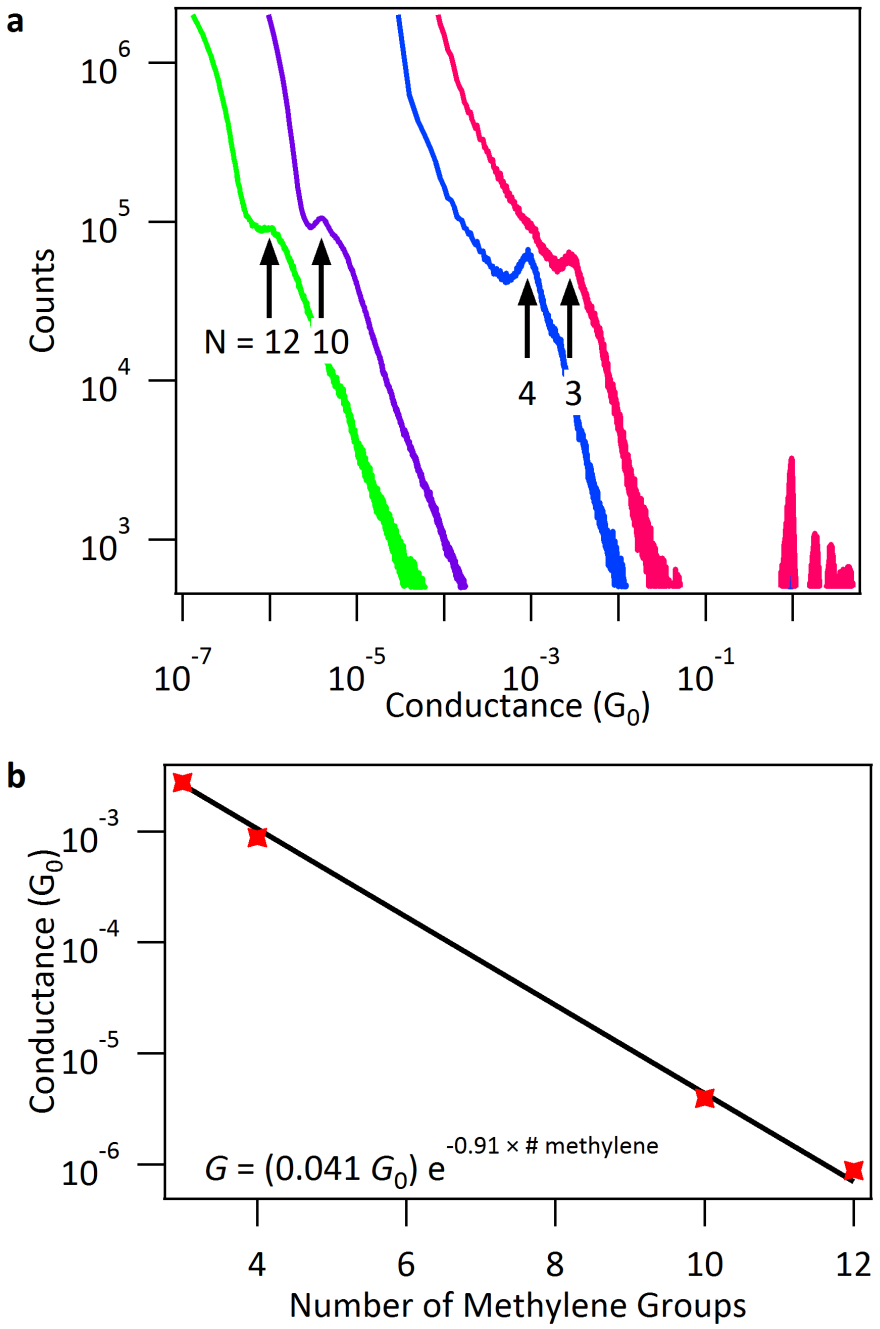

Fig. S2. (a) Conductance histograms (at least 2000 traces each, with linear binning, shown on a log-log scale) for several diaminoalkanes, $NH_2(CH_2)_NNH_2$. (b) Conductance peak positions (extracted by Gaussian fits to each histogram shown in panel (a)) as a function of the number of methylene groups in the molecule. The black line is a linear fit to the logarithm of the conductance as a function of the number of methylene groups, yielding a conductance decay constant of 0.91 ± 0.03 per methylene group.

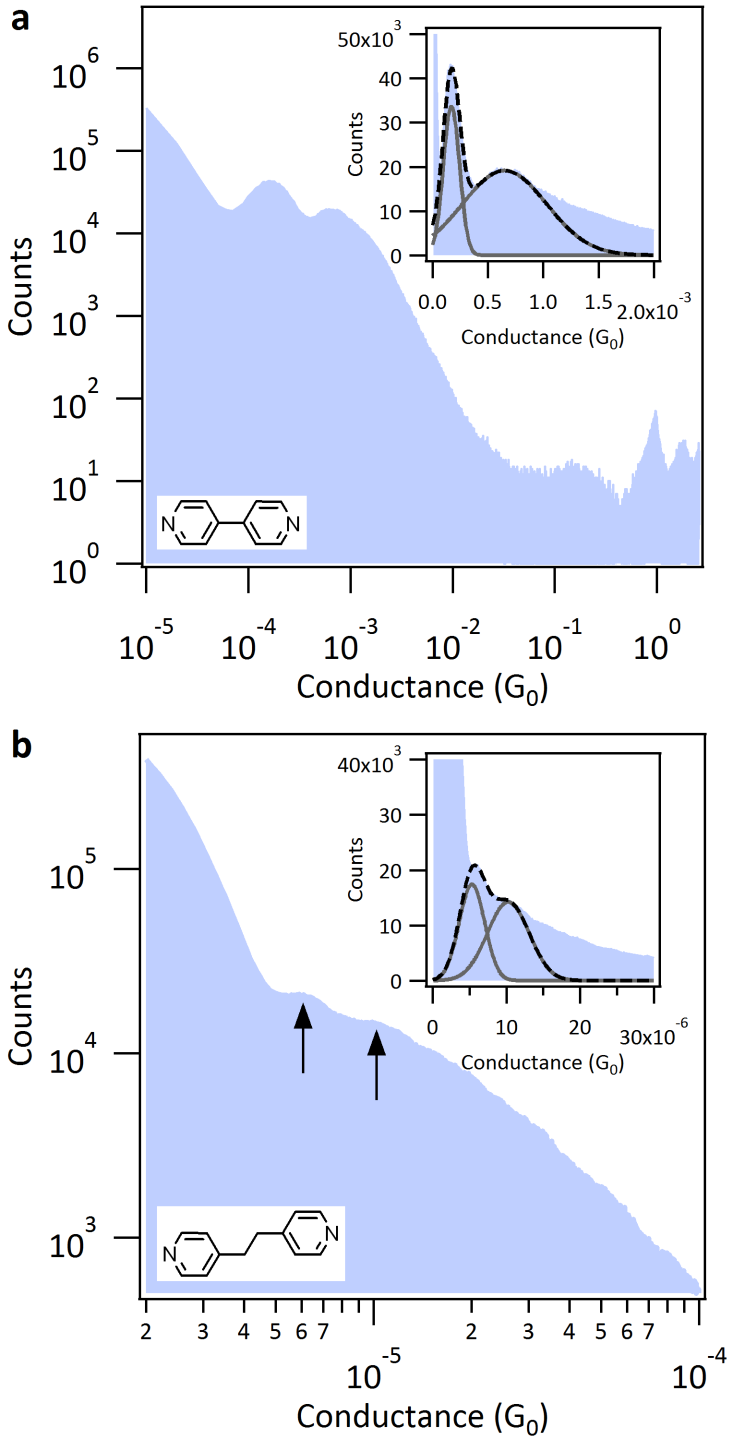

Fig. S3. Conductance histograms (at least 3000 traces) for (a) 4,4'-bipyridine and (b) 1,2-bis(4-pyridyl)ethane. Insets show the same data on a linear scale with Gaussian fits, yielding conductance peak values at (a) $(1.7 \pm 0.1) \times 10^{-4}$ G_0 and $(6.0 \pm 0.2) \times 10^{-4}$ G_0 and (b) $(5.3 \pm 0.2) \times 10^{-6}$ G_0 and $(1.0 \pm 0.1) \times 10^{-5}$ G_0.

Figure S3 shows conductance histograms for (a) 4,4'-bipyridine and (b) 1,2-bis(4-pyridyl)ethane. The doubly-peaked conductance histograms we measure (peak centers are listed in the figure caption) are in good agreement with the results of Kamenetska *et al.*[2] Figure S4 shows a two-dimensional histogram constructed for 4,4'-bipyridine indicating, as seen previously, that this molecule exhibits bi-stable conductance values.

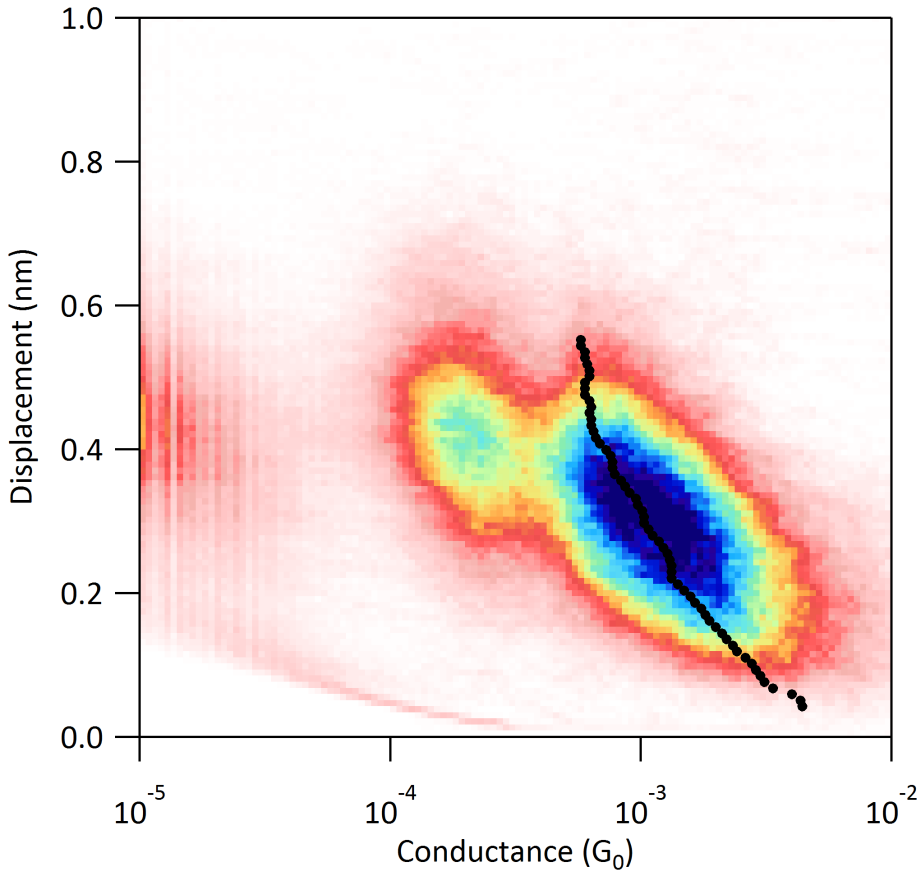

Fig. S4. Two-dimensional histogram for 4,4'-bipyridine from 5000 traces. Black circles mark the fitted peak conductance for each displacement value. Conductance bins are logarithmically spaced.

Additional Data for Dithienylethene Derivatives

In Fig. S5, we show individual traces for the closed (**1c**/**2c**) and open (**1o**/**2o**) forms of the dithienylethene compounds we study in this work. For each data set (thousands of traces), 10-20% of traces show an abrupt step from conductances on the order of 1 G_0 to approximately noise level. These are likely associated with junctions in which the Au metallic contact breaks cleanly without forming a molecular junction. The traces we show in Fig. S5 are representative of 70-80% of the traces (depending on data set) which, from their conductance trend, we associate with the single-molecule junctions of interest. These types of traces give rise to the histogram features we discuss in the main text (although all traces are included in constructing the histograms, with no data selection). A small percentage of traces show more anomalous behaviors of the types that might be associated with trace concentrations of the opposite isometer (e.g., a closed molecule in the solution of open molecules) or multiple molecules in parallel within a junction.

From the sample traces shown in Fig. S5, we note that although measurable current flows through both the open and the closed forms, there is a marked difference in the evolution of the conductance as the electrodes are pulled apart. For the closed forms (left panels), the conductance traces show a clear sloping plateau with both an abrupt beginning and an abrupt end, after which the current drops below noise level. In contrast, the sloping plateaus for the open forms (right panels) show a continuous decrease to noise level. This behavior is also reflected in the two-dimensional histograms in Fig. 3 of the main text for molecule **1o**/**1c**.

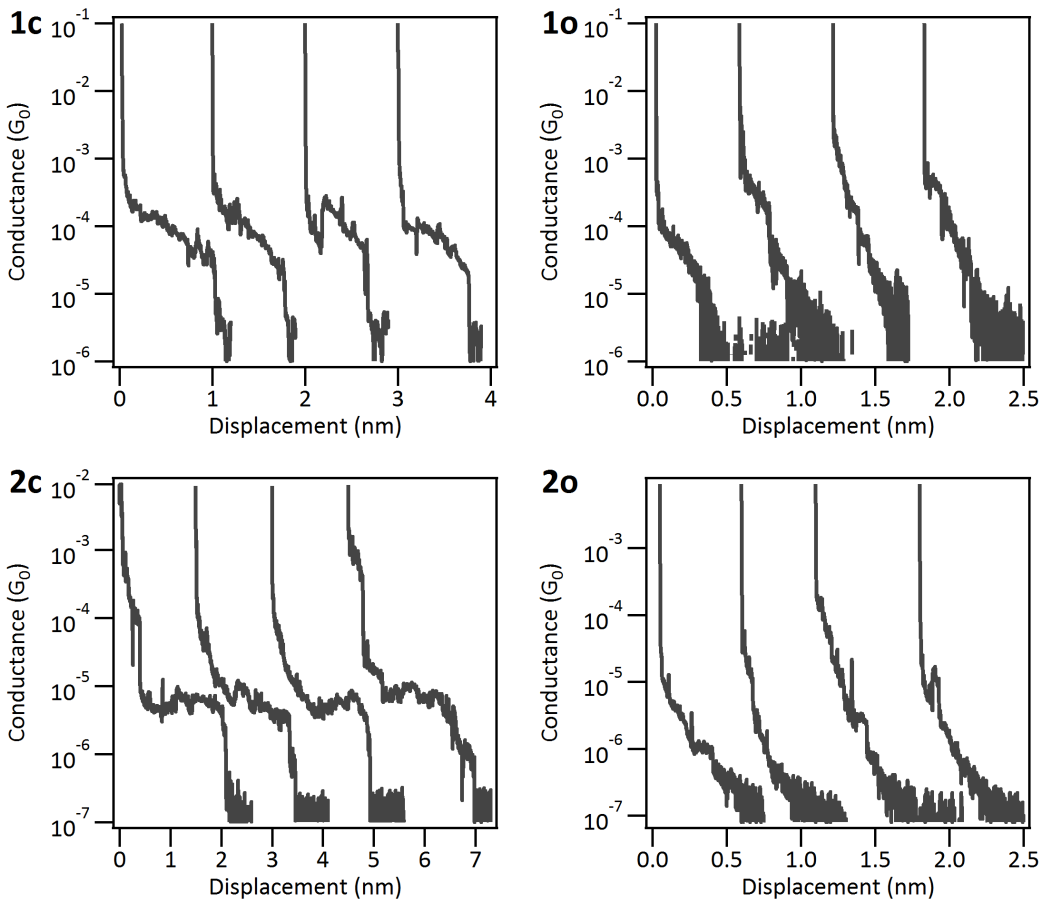

Fig. S5. Examples of individual conductance traces measured for the molecule species as labeled.

Computations

The following are supplemental figures for the *Computations* section of the *Methods* in the main text.

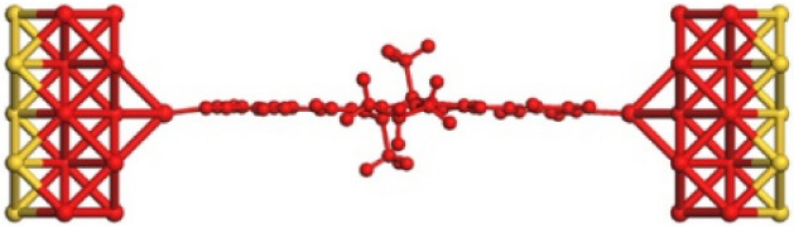

Fig. S6. Simplified molecule-junction configuration used for geometry optimization. Au atoms in red are included in the relaxation; Au atoms in yellow are held fixed.

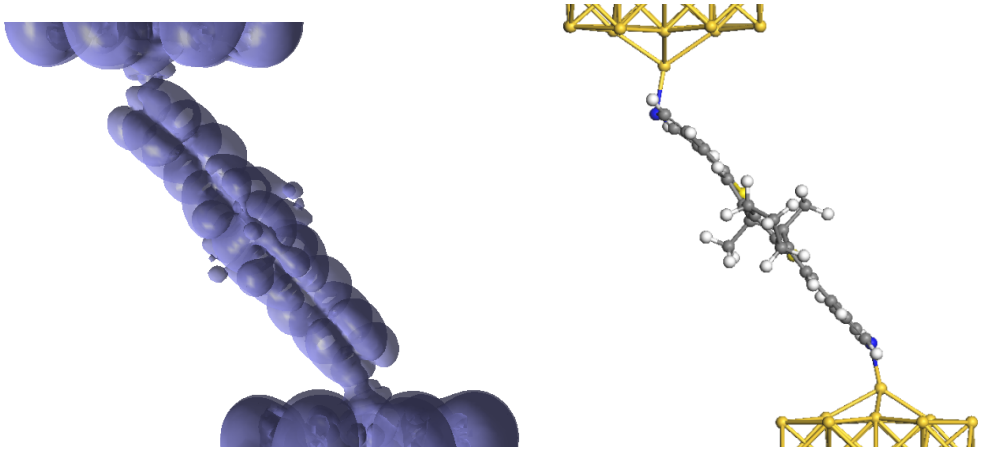

Fig. S7. Local Density of States (LDOS) in the energy window of $E_f \pm 0.05$ eV for compound **1c** shows transmission occurs through the π-system.

The computed conductances (see Fig. 5b in the main text) are significantly larger than the experimental conductances as is typical from DFT calculations, partly due to the well-known inadequacy of approximations for the exchange-correlation functional.[3-7] Nevertheless, the relative magnitude of conductance for **1c** and **1o** is in reasonable agreement with our experimental lower limit for the on-off ratio. We do not see evidence of bi-stable conductance as seen for 4,4'-bipyridine in Ref. 8. Instead, we find that the N-Au bond distance and the conductance change smoothly with electrode separation. Our

calculations appear consistent with the experimental measurements, although we cannot fully rule out the possibility of bi-stability from the range of junction geometries considered here.

References:

(1) Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nano Lett.* **2006**, *6*, 458-462.
(2) Kamenetska, M.; Quek, S. Y.; Whalley, A. C.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Nuckolls, C.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L. *J. Am. Chem. Soc.* **2010**, *132*, 6817-6821.
(3) Di Ventra, M.; Pantelides, S. T.; Lang, N. D. *Phys. Rev. Lett.* **2000**, *84*, 979.
(4) Delaney, P.; Greer, J. C. *Phys. Rev. Lett.* **2004**, *93*, 036805.
(5) Ke, S.-H.; Baranger, H. U.; Yang, W. *J. Chem. Phys.* **2007**, *126*, 201102.
(6) Toher, C.; Filippetti, A.; Sanvito, S.; Burke, K. *Phys. Rev. Lett.* **2005**, *95*, 146402.
(7) Sai, N.; Zwolak, M.; Vignale, G.; Di Ventra, M. *Phys. Rev. Lett.* **2005**, *94*, 186810.
(8) Quek, S. Y.; Kamenetska, M.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L. *Nat. Nano.* **2009**, *4*, 230-234.